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(54) **Edible fats.**

(57) Hard butters for confectionary are obtained by separating mid- and oelin- fractions and preferably also a stearin-fraction, from a vegetable fat containing substantial amounts of symmetrical disaturated triglycerides of $C^{16}/C^{18}$ fatty acids and rearranging the gylcerides in a mixture of the olein fraction with a substantially saturated $C^{16}/C^{18}$ fat, preferably the stearin fraction, in the presence of a catalyst, preferably a lipase enzyme, which is selectively active in the 1, 3-positions only of glycerides, to provide increased amounts of symmetrical disaturated triglycerides which may be fractionated from the rearranged product.

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# EDIBLE FATS

This invention relates to hard butters and their preparation from edible fats.

The eating quality of chocolate fat and other hard butter compositions containing cocoa butter is attributable to the presence in this fat of a high proportion of symmetrical disaturated triglycerides, principally the 2-oleyl glycerides of palmitic and stearic acid. Various substitute fats which have been proposed as an alternative to this expensive fat similarly contain more or less substantial quantities of these triglycerides. Processes for the production of cocoa butter substitutes and extender fats from these alternative sources generally include fractionation steps in which these more valuable glycerides are separated from others with less desirable melting attributes, notably trisaturated glycerides and mono-saturated and tri-unsaturated triglycerides, but also asymmetric disaturated glycerides, where these can be separated. The separation is usually effected by fractional

crystallisation, particularly from a solvent such as acetone or hexane, the more highly saturated glycerides being removed in a higher-melting or stearin fraction, and the more highly unsaturated glycerides being removed in a lower-melting or olein fraction. These less desirable fractions may constitute as much as half the original fat and command a much lower premium than the hard butter fraction.

Interesterification of fats and glyceride oils by methods using enzyme rearrangement catalysts have been described in GB 1577933. EP 69599 discloses fractionation of fats with rearrangement of the glycerides in the fractions obtained, followed if desired with fractionation of the product, to recovery more highly symmetrical glycerides, particularly for the preparation of cocoa butter replacement fats.

The present invention proposes a process for the recovery of hard butters from vegetable fats, in which a vegetable fat containing substantial amounts of symmetrical disaturated triglycerides of $C_{16}$ and $C_{18}$ fatty acids is fractionated to recover the said glycerides by separating at least a more highly unsaturated, lower-melting olein fraction, which is mixed with a substantially saturated $C_{16}/C_{18}$ triglyceride fat, preferably by re-combining with an upper-melting , stearin fraction also separated from the vegetable fat, and the mixture interesterified in the presence of an enzyme catalyst which is preferably selectively active in the outer positions only of glycerides, i.e. the 1- and 1,3-positions or alpha-positions of the glycerides, to yield further quantities of symmetrical disaturated glycerides.

Since the greatest proportion of the olein fraction consists of glycerides having an unsaturated fatty acid residue in the 2-position, all these are theoretically capable of conversion by interesterification under the influence of the enzyme catalyst to symmetrical disaturated triglycerides, provided only that sufficient glycerides are present in the blends, for example in the upper-melting or stearin fraction with which it is preferably combined, containing saturated fatty acid residues in the alpha or 1,3-positions that are vulnerable to the catalyst for effecting interesterification with the more highly unsaturated glycerides. For example, trisaturated glycerides may undergo interesterification with tri-unsaturated glycerides to provide 1-saturated di-unsaturated glycerides and these in turn to 1,3-disaturated glycerides, under the influence of the selective action of the catalyst. The trisaturated glycerides themselves convert correspondingly to asymmetric disaturated mono-unsaturated glycerides and symmetric di-unsaturated glycerides, i.e. 1,3-diunsaturated, 2-saturated glycerides.

The interesterified glycerides may be separated as in conventional fractionation processes, to recover a fraction consisting essentially of symmetrical disaturated glycerides for use as a cocoa butter replacement fat. The more highly unsaturated glycerides in the interesterification mixture, including in particular the symmetrical 1,3-di-unsaturated glycerides, form a lower-melting oleine fraction. Any unreacted trisaturated glycerides may be separated if necessary in a top fraction, and recycled for further interesterification with any asymmetric disaturated glycerides, whether these appear in a stearin or olein fraction separated from the symmetrical disaturated fraction.

The mixture of interesterified glycerides may be separately fractionated or recombined with feedstock in the fractionation step of the process. In a continuous operation in which feedstock is introduced to, and a symmetrical disaturated glyceride fraction removed from, circulation through fractionation and interesterification units, the feedstock may be introduced into either unit and may thus be fractionated first, in admixture with the entire interesterification output, or interesterified first together with the recycled interesterified fractions from which the symmetrical disaturated glycerides have been removed. In continuous operations in which feedstock is introduced and a symmetrical disaturated fraction removed, a purge may also be necessary of the symmetrical di-unsaturated glycerides to avoid build-up of this intractable material in the recycled composition. Rearrangement catalyst may also be used to convert this material and return it in a more tractable form, for example, a non-selective catalyst, a 2-selective catalyst, or one which is selectively active to saturated but not unsaturated fatty acid residues. A particular advantage of continuous operation is that the interesterification need be of relatively short duration since the interesterification can be incomplete for each pass through the unit. Enzyme interesterification is generally substantially slower than interesterification under the influence of inorganic catalysts which are also used at much higher temperatures. By continuous recycling however, the residence time in the interesterification step need be sufficient only to provide a significant improvement in the yield of the desired glycerides, without necessarily reaching equilibrium.

The invention also includes recovery of the product from the rearrangement step, without fractionation or recycle, particularly for the preparation of hardstock fat

which is then blended with liquid glyceride oils, to provide a composition suitable for margarine or other emulsion food spreads, or the fat may be used in ice-cream.

Fractionation steps carried out in accordance with the invention may be conventional, either by solvent fractionation using acceptable solvent, for example acetone, hexane or nitroparaffins or ambient gases in liquid condition under pressure. Fractionation may also at least in part be dry without solvents and may then be aided as in the so-called Lanza process, by the use of surfactant aqueous dispersions for facilitating separation of liquid and solid phases during fractionation. Preferably the fractionation is carried out however in acetone at temperatures from 15 to -5°C or in hexane at temperatures from 10°C to -20°C.

Suitable enzymes which are active to catalyse interesterification only in the outer positions of glyceride molecules include, for example, Aspergillus niger and Mucor michei. These enzyme catalysts ensure that the unsaturated fatty acid residue in the 2-position of the glycerides of the lower-melting fraction remain unaffected by the interesterification, to provide a foundation for the production in that reaction of the desired symmetrical disaturated glycerides for the mid-fraction. Enzyme catalysts are particularly preferred for this process, but other catalysts may of course be adopted provided they show selective interesterification at the alpha-positions only. The interesterification reaction may be carried out in solvents which leave the catalyst unaffected, particularly hexane for enzyme catalysts, or without solvent and the reaction may be batchwise or continuous, the catalyst in the latter event being preferably fixed in a reaction vessel through which

the reaction burden comprising the mixed upper- and lower-melting fractions are passed. Enzyme catalysts may be pre-activated by contact with water and they may be supported on a suitable carrier, as described in our patent specification GB 1577933. The water content may be obtained during the reaction, to predetermined limits in accordance with our patent specification (GB abandoned but EP 64855) by the use of humectants and/or other means for removing water from the reaction phase. The water content is preferably not more than 2% of the reaction mass, including solvent, and particularly not more than 1%. In particular, the water activity $A_w$ is preferably less than 50% during reaction. Enzyme catalysts may also however be used in polyhydric alcohol solution to maintain a very low water content. The water content is preferably low enough to minimise the extent of hydrolysis taking place with the production of partial glycerides. These may however be removed by selective adsorption means using silica-type adsorbents.

Suitable fats include in particular palm oil but also shea, sal, pentadesma oil and of course cocoa butter itself, may all be processed in accordance with the present invention. Vegetable oils and fats are used since these contain an abundance of unsaturated fatty acid residues in the 2-position of their glycerides. Mixtures of oils and fats may be used and a fat which is deficient in trisaturated glycerides may be mixed with another containing them, or hydrogenated to provide sufficient for the interesterification reaction. Preferably the oils are refined before use as feedstock in the present invention and both neutralised and un-neutralised oils and fats may be used.

EXAMPLE

Equal parts by weight of olein and stearin fractions obtained by the acetone fractionation of palm oil to remove a palm mid-fraction, were combined and the blend was dissolved in 3 times its own weight of hexane and interesterified using as interesterification catalyst a 1, 3-specific enzyme derived from a Mucor miehei organism supported on a diatomaceous earth in a packed bed reactor and activated with water before use. The miscella, containing 500ppm of water, was fed at 3 litres per hour through the reactor which contained 0.7 kg of catalyst. The residence time in the reactor was approximately 30 minutes and the reaction was carried out at 55°C.

Solvent was distilled from the product which was then recrystallised from acetone, first at 20°C and then at 5°C to recover a mid-fraction, this is compared in the accompanying Table with a sample of mid-fraction obtained by crystallisation from unmodified palm oil. The composition is also given in the Table of the feedstock blend and its components. The olein and stearin fractions derived from the reaction product were found to be essentially similar in composition to these, the triglyceride analyses being determined by silver-phase HPLC methods.

TABLE

| | SSS | SUS | SSU | SLnS | SUU | Others |
|---|---|---|---|---|---|---|
| Olein fraction: | 0 | 12.3 | 4.9 | 10.9 | 45.0 | 27.0 |
| Top fraction: | 77.4 | 18.2 | 2.6 | 1.4 | 0.4 | 0 |
| Blend: | 42.0 | 15.9 | 3.7 | 5.5 | 20.7 | 12.3 |
| Product: | 22.8 | 22.6 | 25.0 | 7.6 | 20.1 | 11.8 |
| Mid-fraction ex. Product: | 4.3 | 43.7 | 31.2 | 6.2 | 11.4 | 3.2 |
| Do. ex palm oil: | 5.1 | 71.7 | 2.0 | 8.0 | 6.2 | 2.1 |

Claims

1. Process for the recovery of hard butter from vegetable fats wherein a vegetable fat containing substantial amounts of symmetrical disaturated triglycerides of $C_{16}$ and $C_{18}$ fatty acids is fractionally crystallised to recover the said glycerides and at least a more highly unsaturated oleine fraction, wherein the latter fraction is mixed with a substantially saturated glyceride composition and the mixture interesterified in the presence of an interesterification catalyst which is preferably a lipase enzyme selectively active in the 1- and 3-positions only of glycerides, to yield further quantities of symmetrical disaturated triglycerides and if desired separating these from the product by fractional crystallisation.

2. Process according to Claim 1 wherein the substantially saturated glyceride composition is recovered by fractional crystallisation from the said vegetable fat.

3. Continuous process according to Claim 1 or 2 comprising fractionation and interesterification stages between which reaction burden is circulated, into which feedstock comprising the said vegetable fat is introduced and from which a symmetrical disaturated glyceride fraction is removed.

4. Continuous process according to Claim 2 wherein an additional fraction is removed comprising 2-saturated mono- and di-unsaturated triglycerides.

5. Process according to any of the preceding claims at least part of which is carried out in solution in an organic solvent.

6. Process according to Claim 5 the fractionation part only of which is carried out in organic solvent.

7. Process according to Claim 5 or 6 wherein a solvent is used comprising acetone or a lower paraffin.

8. Process according to any of the preceding claims wherein the vegetable fat comprises aceituno, sal, shea, mango, kokum or phulwara fat.

9. Process according to claim 2 wherein the fat comprises palm oi.

10. Hard butters whenever prepared by a process as claimed in any of the preceding claims.

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